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Analysis of CL-20 in Environmental Matrices: Water and Soil

Steven L. Larson, Deborah R. Felt, Lynn Escalon,
Jeffrey D. Davis, and Lance D. Hansen

August 2001

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Preface

The work reported herein was conducted by the U.S. Army Corps of Engineers (USACE) at the Engineer Research and Development Center (ERDC), Vicksburg, MS. This applied research project was made possible by USACE research funded by the Army's Environmental Quality Technology Research Program, Project AF 25.

This report was prepared by Dr. Steven L. Larson, Dr. Jeffrey D. Davis, and Mr. Lance D. Hansen of the Environmental Engineering Branch (EEB), Environmental Laboratory (EL), ERDC; Deborah R. Felt, Applied Research Associates, Inc.; and Lynn Escalon, ASI Corporation. The Environmental Chemistry Branch, EL, performed chemical analyses.

This report was technically reviewed by Robert Jones and Charles White, EL. In addition, the authors gratefully acknowledge Dr. John Cullinane, ERDC, for his guidance and support.

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1 Introduction

The environmental consequences of industrial production of such well-known energetic materials as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitrotoluene (TNT) are well documented. There are over 17,000 sites at Department of Defense (DoD) installations, both active and inactive, that potentially require environmental cleanup. Energetics-contaminated soil and groundwater make up a considerable portion of the contamination at these sites. TNT, RDX, and HMX are the most prevalent sources of contamination at these and Department of Energy (DOE) sites because of their widespread use in military development and testing.

The recently synthesized compound hexanitrohexaazaisowurtzitane (HNIW) (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.05,9.03,11] dodecane), also known as CL-20, is the subject of numerous advanced research and development (R&D) studies seeking an alternative to currently used explosives (Nielsen 1991, 1997). Several studies and calculations have been carried out to evaluate the potential of CL-20 for military applications (Russell et al. 1992, Kodama et al. 1994). This work includes explosive performance, sensitivity, and response to one-dimensional shock loading (Simpson et al. 1997). Additionally, CL-20 has been investigated in terms of its crystal and molecular structure (Nielson 1991, 1997).

The structure of CL-20 is shown in Figure 1. The structures of TNT and RDX are also shown for comparison. CL-20 is referred to as a cage compound because it resembles two RDX rings joined at several carbon atoms.

Propellants and explosives formulations using CL-20 are expected to have better performance in terms of specific impulse, burn rate, ballistics, and detonation velocity compared to RDX and HMX. In addition to improved performance, CL-20 meets stringent munitions sensitivity requirements. Because CL-20 contains no halogens, its combustion products are more environmentally acceptable than those derived from the combustion of propellants made with ammonium perchlorate. The widespread, high-level interest in CL-20 has resulted in an increase in its industrial production up to several thousands of pounds per year. To date there have been no studies on the environmental impact of CL-20 and its degradation products. Concerns regarding the environmental fate of CL-20 are arising because of the potential for deposition within soil or water systems resulting from CL-20 manufacture and the loading and use of munitions containing CL-20. Before full-scale production begins, a thorough investigation

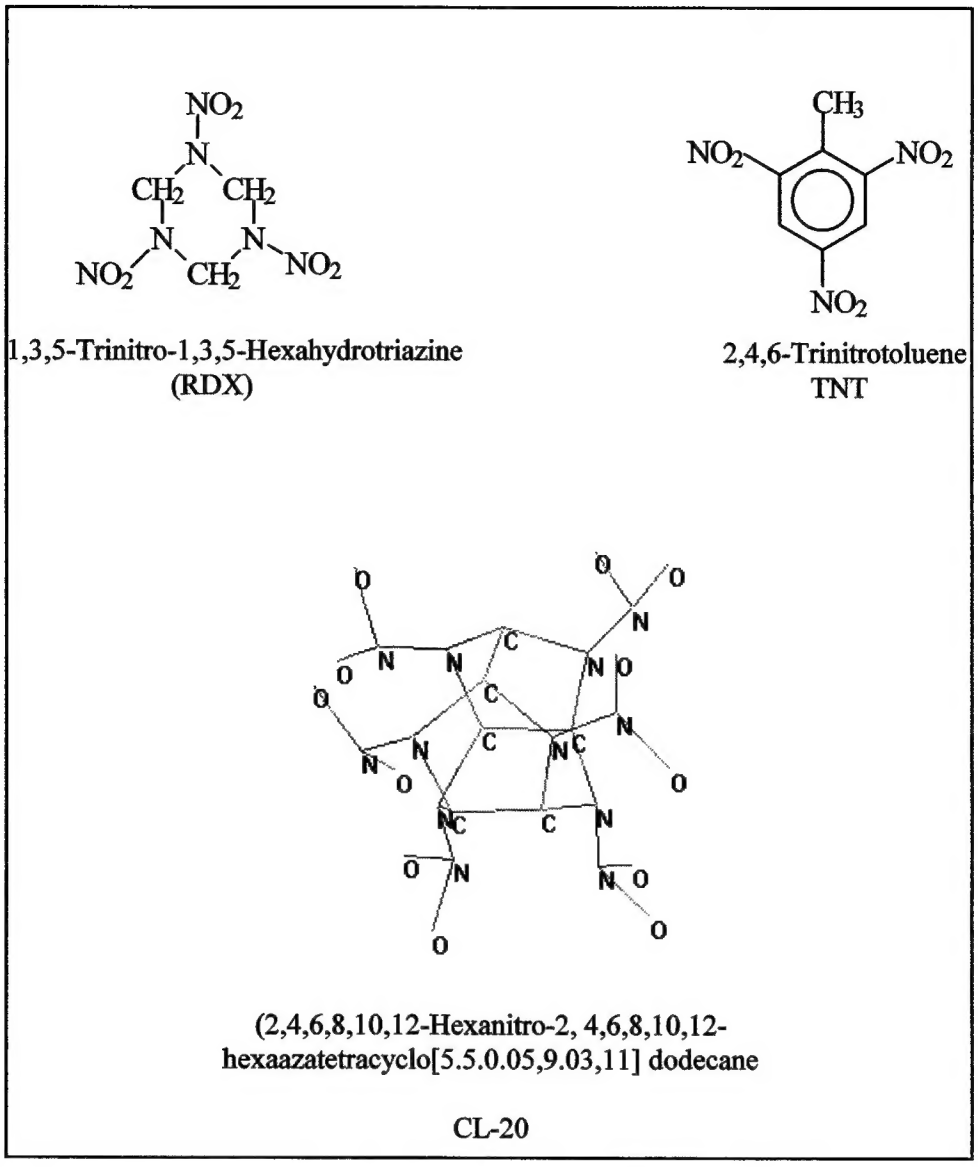

Figure 1. Molecular structures of CL-20, TNT, and RDX

of CL-20's environmental fate, transport, and effects, along with remedial alternatives for cleanup of CL-20 in soils and waters, is warranted.

A number of technologies have been used to clean up contamination from traditional explosives (TNT, RDX, nitrocellulose, tetryl, and others) in water and soil (Binks 1995, Crawford 1993, Dillert et al. 1995, Arienzo 1999). These techniques include chemical, photochemical, phytological, physical, thermal, aerobic, and anaerobic microbiological treatment technologies, along with natural attenuation and phytoremediation. Much interest has been generated recently in developing analytical methods for the determination of explosives, by-products of explosives manufacture, and explosives degradation products. Analytical techniques for the detection of nitroaromatic breakdown products have been developed and refined over the past 15 years (EPA 1994).

High performance liquid chromatography (HPLC) equipment has been used to separate the compounds produced by the degradation of CL-20. HPLC methodology was employed to investigate and develop sample preparation and techniques for analysis of CL-20 in various matrices.

2 Experimental Methods

The methods used to detect CL-20 in a variety of environmental samples require matrix-specific sample preparation, separation by reverse-phase high performance liquid chromatography, and ultraviolet detection. The analytical systems described in this report are identical to those that are required to perform USEPA SW-846 Method 8330 for the determination of explosives in waters and soils. Samples resulting from research projects are often limited in mass and volume. The method developed for the analysis of CL-20 in these matrices was designed to reduce the amount of material that a laboratory would have to acquire in order to analyze for CL-20. The instrumental methods are outlined below.

Analytical System

The equipment used in sample preparation included centrifuge and centrifuge tubes (3000 rpm), syringes and filters, volumetric flasks of various sizes, automatic pipettes, and autosampler vials.

The HPLC system consisted of a Waters 610 fluid unit pump capable of achieving 6000 psi, a Waters 717 plus autosampler including a 200-µL loop injector, a Waters 486 tunable UV absorbance detector monitored at 245 nm, a Waters 410 diode array UV absorbance detector, and Millenium 2.1 chromatography software (Waters Chromatography Division, Milford, MA). A Supelco LC-18 reverse-phase HPLC column 25 cm x 4.6 mm (5 µm inside diameter), catalog # 5-8298 was used as the primary column, and a Supelco LC-CN reverse-phase HPLC column 25 cm x 4.6 mm (5 µm inside diameter), catalog # 5-8231 was used as a confirmation column. The use of both C18 and CN columns allowed this system to produce interference-free determinations. The appropriate pre-column, Novapak C-18 catalog # WAT015220 or Novapak CN, catalog # WAT020800 (Waters Chromatography Division, Milford, MA), was utilized.

Sonication extractions were performed using a temperature-controlled ultrasonic bath; the temperature did not exceed 30 °C. The filtration system used for sample preparation consisted of a disposable LurLoc syringe and disposable 0.50-µm Teflon filter cartridges. Solid-phase cartridges used for sample concentration were Waters SepPak Vac cc (500 mg) Porapak RDX cartridges, catalog # WAT047220.

Reagent-grade inorganic chemicals were used in all tests. Unless otherwise indicated, all reagents conformed to the specifications of the Committee on Analytical Reagents of the American Chemical Society. The solvents used in this method were acetonitrile (CH_3CN, HPLC grade) and methanol (CH_3OH, HPLC grade). Calcium chloride ($CaCl_2$) was used as an aqueous solution at 5 g/L. The water used was organic-free reagent water (18 mΩ Milli-Q). The HPLC mobile phase [1:1 (v/v) methanol/reagent water] was prepared by measuring 500 mL of each and combining them prior to filtration. A vacuum filtration system from Millipore with 0.22-μm filters was used for degassing the mobile phase and removing particulate matter.

Matrix

This method can be used for the determination of CL-20 and its breakdown products in a broad range of matrices. It easily accommodates the measurement of CL-20 breakdown products in water samples ranging from distilled water to seawater to heavily contaminated wastewaters. Mass quantification of extractable CL-20 and its breakdown products in soil is also possible. To obtain the method detection limits that are attainable for other explosives compounds, samples are prepared using solid-phase extraction to provide a concentrated extract for HPLC analysis. It is also possible to attain method detection limits of extractable CL-20 from soil that are analogous to the current USEPA SW-846 method 8330.

Sample Preparation

High concentrations in water. Water samples were prepared for the high-level method by adding 5 mL acetonitrile to 5 mL of sample. Method blanks were generated by adding 5 mL of acetonitrile to 5 mL of Milli-Q water, and laboratory control samples were prepared by spiking 5 mL of Milli-Q water with 5 mL of acetonitrile. The samples were then filtered using a 0.45-μm Millipore Millex-SR Teflon filter and placed in an autosampler vial for analysis. All samples were refrigerated at 4 °C.

Low concentrations in water. For the low-level method of extraction, water samples were extracted by a solid-phase extraction procedure using a vacuum manifold and solid-phase cartridges [Waters SepPak Vac cc (500 mg) Porapak RDX]. The cartridges were conditioned with 10 mL of acetonitrile followed by 15 mL of Milli-Q water. After conditioning, 500 mL of sample was passed through the cartridge until no sample was visible in the cartridge (to dryness). The samples were then eluted off the cartridges using 5 mL of acetonitrile and were collected in centrifuge tubes. Method blanks were prepared by passing 500 mL of Milli-Q water through the cartridge, and laboratory control samples were prepared by passing 500 mL of spiked Milli-Q water through the cartridge. The concentrated extract was diluted 1:1 (v/v) with reagent-grade water.

Soils. Soil samples were prepared for analysis by the following procedure: the soil sample was thoroughly mixed to achieve maximum homogeneity prior to sub-sampling. Approximately 5.0 ± 0.5 g of wet sample was weighed into a 20-mL glass vial with a Teflon-lined cap, and the weight was recorded. Samples and associated quality control samples were spiked with surrogate and matrix spiking solutions. Acetonitrile (10 mL) was added, and using a vortex mixer, samples were swirled for one minute and then placed in a cooled ultrasonic bath for 18 hours. After sonication, samples were allowed to settle for 30 minutes. Representative aliquots (5 mL) of supernatant were removed using 5-mL pipettes with disposable tips and were placed into 20-mL vials. Portions (5 mL) of calcium chloride solution (5% by weight) were added to the 5-mL samples of supernatant. The resulting samples were then filtered and analyzed by HPLC.

To determine the percentage of solids of the original soil samples, representative samples (2-4 g) of the wet material were placed in disposable weigh dishes, and the weights were recorded. Samples were air dried at room temperature and weighed again after drying.

Concentration Ranges

The tested concentration range depends on the matrix in which CL-20 and its degradation products are being measured. Standards dissolved in organic solvents and injected directly into the HPLC can be tested in the concentration range of 0.04 to 4.0 μg/mL. Natural waters spiked with standards can be tested in the concentration range of 0.1 to 20 μg/mL using the high-level method and in the concentration range of 0.5 to 200 ng/mL using the low-level method. Clean soils spiked with standards can be tested in the concentration range of 0.10 to 20 μg/g. The testable concentration range will vary considerably depending on the matrix encountered. Samples that contain high concentrations of other contaminants may have much higher background levels, and detection limits may be considerably higher.

Interferences

There is always a possibility that an extract may contain a compound that absorbs UV light at the wavelength used for CL-20 detection and would elute from the analytical column at a similar time as CL-20. However, the use of both C18 and CN columns, which have dissimilar retention characteristics, allows this chromatographic system to significantly reduce the frequency of interferences on both columns. Comparison of the signal amplitude for peaks with the appropriate retention times for CL-20 serves to identify interfering compounds in specific extracts.

Safety

Many nitramine and nitroaromatic explosives, including Cl-20, are suspected carcinogens. Some degradation products of nitroaromatics are more toxic than their parent compounds. The nitrosoamines are a class of organic contaminants that are also known carcinogens (Baumgarten and Curtis 1982). The compounds formed during the degradation of CL-20 have not been identified, and the possible health effects of these compounds are unknown. Good laboratory technique and protective equipment are required during the entire analysis as a result of both the safety risk associated with the analyte and the need to minimize background current arising from contamination. Protective equipment includes impermeable latex gloves, safety glasses, and fume hoods. Standards and eluents should be disposed of in accordance with approved regulatory practices.

3 Results

The development of an analytical method for CL-20 determination in waters and soils began by identifying a chromatographic system that could separate CL-20 on both the primary and secondary analytical columns. A standard of CL-20 material was obtained from the Naval Air Warfare Center Weapons Division for spiking into a simulated extract.

Figure 2 shows chromatograms acquired with CL-20 prepared with purified standards. These solutions were prepared using reference standards in 50 percent acetonitrile and 50 percent distilled water. Baseline separation (separation of the CL-20 from other peaks observed during the analysis where the baseline is achieved between the analyte peak and other peaks) was achieved on both columns.

The elution times for CL-20 were significantly longer on the CN column than on the C18 column. Generally the non-polar C18 analytical column allows the most polar compounds to elute first and the non-polar compounds to elute later. The CN column contains silica coated by a cyanide derivative that is more polar than the C18 column. As a result the polar compounds are retained on this column while the non-polar compounds elute more quickly.

The use of two columns with different retention characteristics serves two functions. It helps confirm the peak identified on the primary column by identifying the same compound at the same concentration and distinctive retention time on the second column. The likelihood of an unknown interfering peak matching retention times is quite high on a single column, but not on two columns with dissimilar solid phases. The dual column technique also serves to remove known interferences.

Another technique that can be used to confirm that the peaks are diagnostic of CL-20 is matching the UV-visible spectrum for the peak with the known spectrum of CL-20. A common analytical instrument used for HPLC detection is the photo-diode array spectrometer, which is capable of measuring a complete UV-visible spectrum at any point along a peak. The spectrum of the CL-20 compound can be obtained during elution using a photo-diode array detector. Figure 3 contains the UV spectrum associated with the peak detected at 245 nm that was separated on the CN column. The figure illustrates a maximum at 230 nm and no absorbance evidenced between 280 and 400 nm.

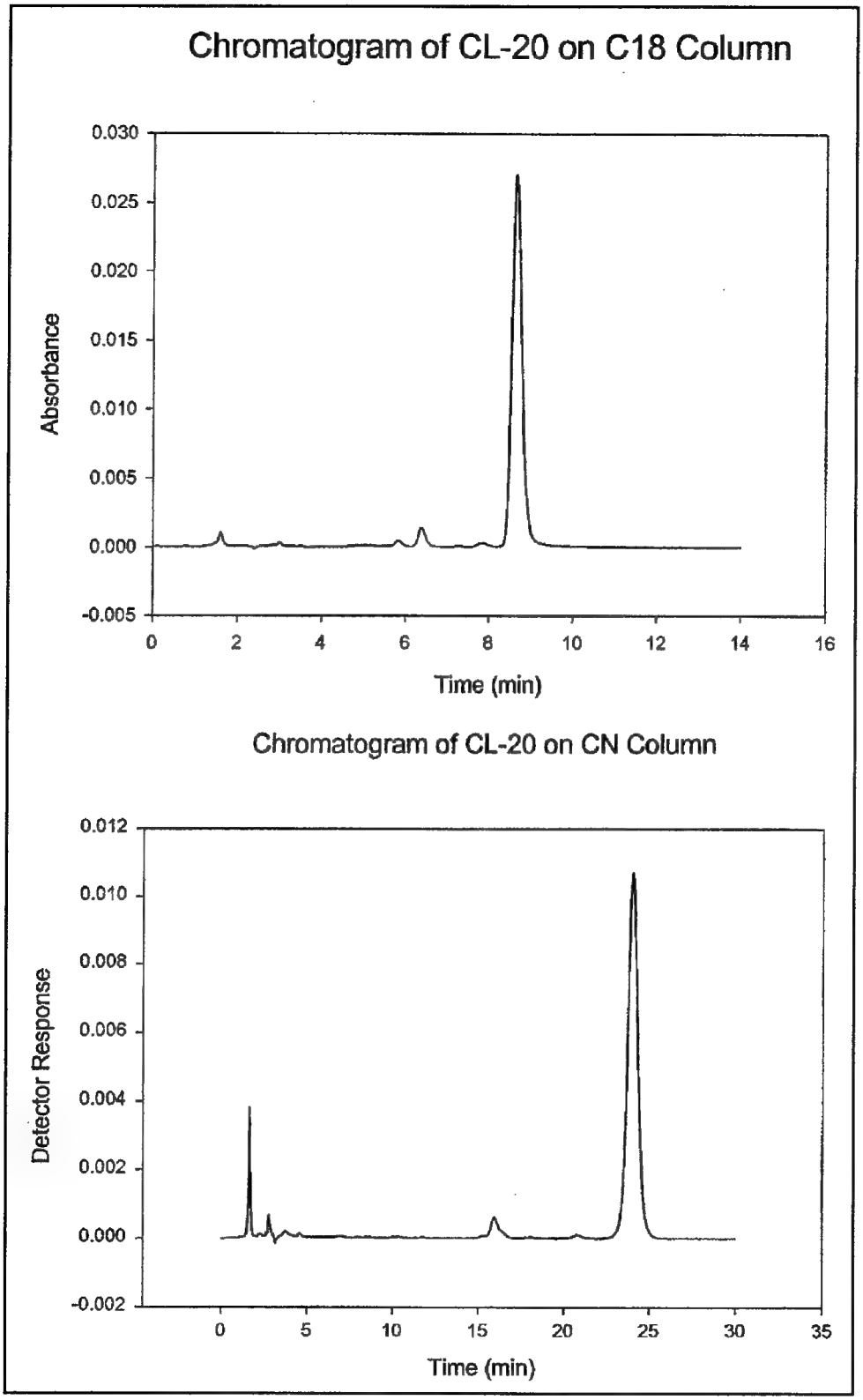

Figure 2. Chromatograms for CL-20 using the C18 and CN columns

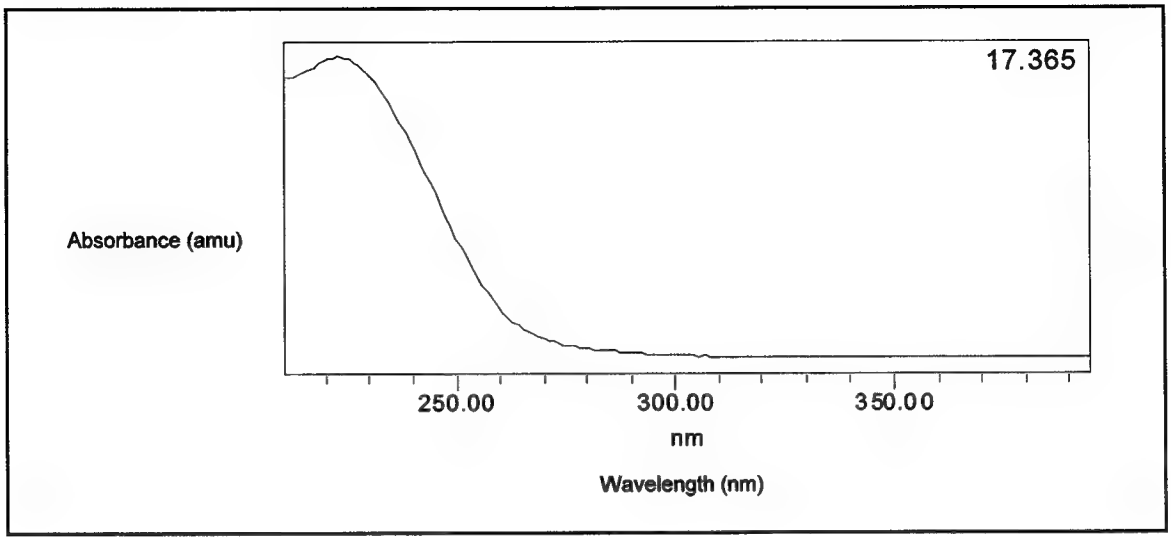

Figure 3. Ultraviolet spectrum of CL-20 from CN column at 17.365 min retention time

Using the technique to determine the concentration of CL-20 in the extracts from soil and water requires a correlation between the detector response and a set of samples with known CL-20 concentrations. This instrument calibration results in a set of paired data for the concentration and the detector response that can be plotted and fit to an algebraic correlation. A series of extracts using purified reference standards at known concentrations was prepared and analyzed to determine this correlation. Figure 4 shows the CL-20 calibration curves for the C18 and CN columns. Excellent linearity is achieved over three orders of magnitude of the concentration range (R^2 values for least-squared linear curve fit are 0.9998 and 0.9983). The difference in slopes can be attributed to the retention time differences between the two columns. Peak heights, instead of peak areas, were used to quantitate chromatographic features because this method yielded more consistent results. The retention time of CL-20 is much longer on the CN column, 24 min compared to 8.75 min on the C18 column. Longer retention time cause chromatographic peaks to broaden, which decreases the peak heights, causing a gentler slope for the standard curve. Figures 5 and 6 show a set of chromatograms produced during preparation of the calibration curves. Retention times are stable throughout the three orders of magnitude in the calibrated concentration range.

Because the use of explosives often results in soil and water contamination in which a number of explosive compounds are present in mixtures, the method must be able to quantitiate CL-20 in the presence of these other common compounds. Both TNT and RDX are explosive-based compounds that are common contaminants in both soil and water. Figure 7 shows CN and C18 chromatograms that exhibit the proposed method's ability to separate the CL-20 from both RDX and TNT.

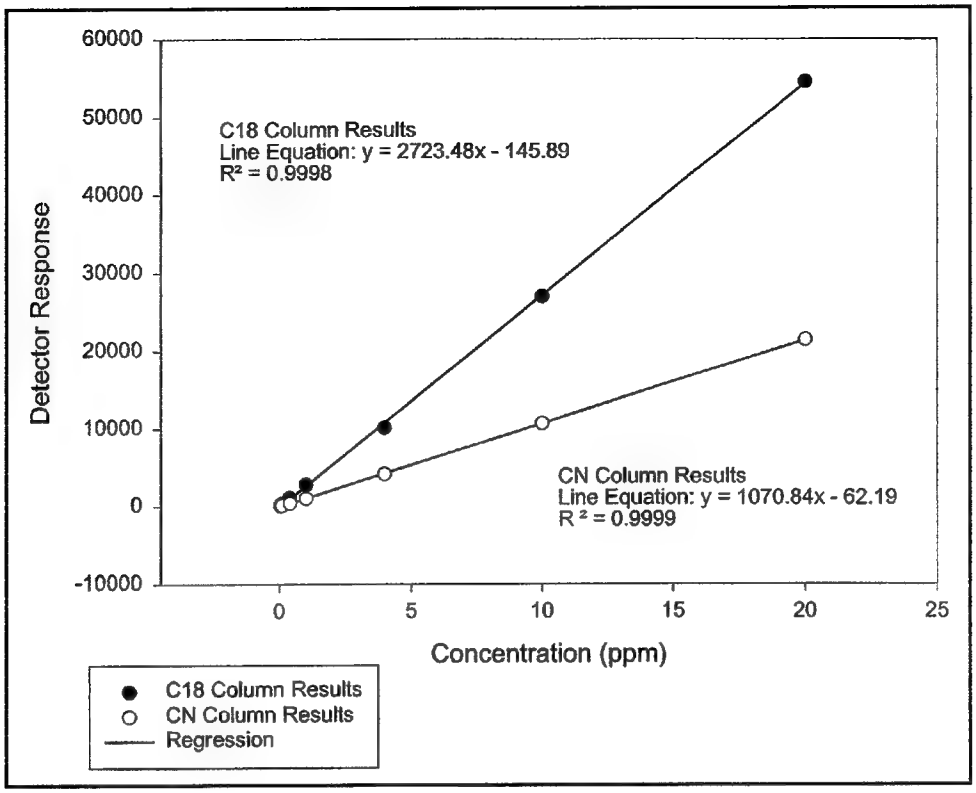

Figure 4. CL-20 calibration curves on C18 and CN columns

In accordance with the requirements of USEPA SW846, the method detection limits (MDL) and laboratory reporting limits (LRL) were determined for the quantitation of CL-20 in the three matrices/extracts described in this report. Table 1 contains the results of seven replicate runs near the data reporting limit as well as the statistical interpretation of those results. As can be seen, precision is good for the replicate analysis in both water and soil matrices. The MDLs are 0.10 ppb for concentrated extracts in water, 17.1 ppb for unconcentrated extracts in water, and 33.93 ppb for extracts in soil. The LRLs are five times the MDL values, or 0.49, 85.48, and 169.64 ppb, respectively.

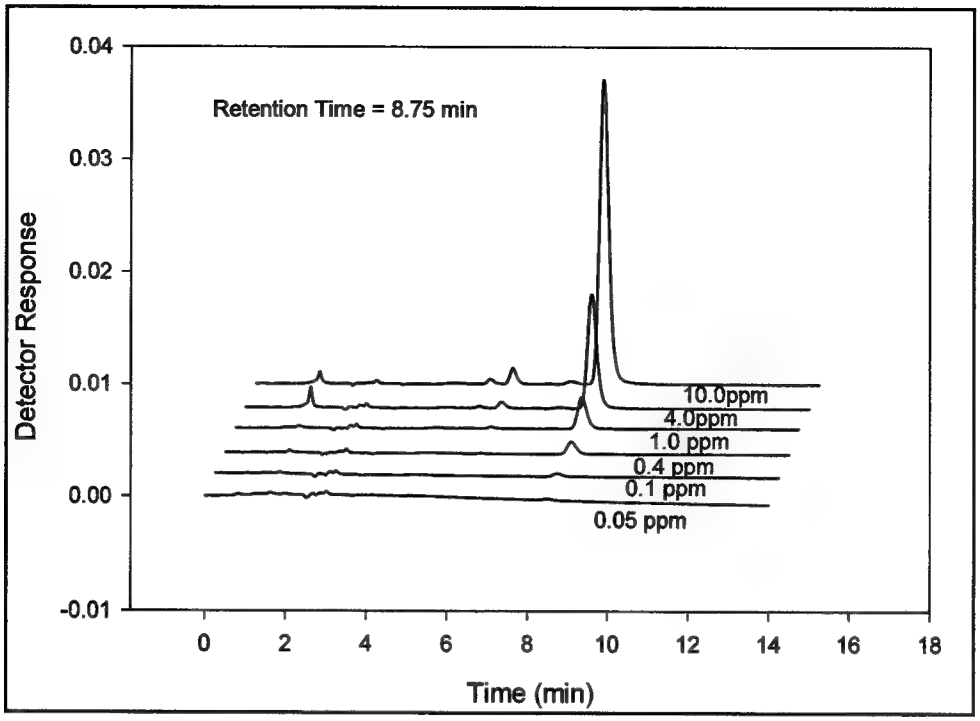

Figure 5. CL 20 calibration on C18 column

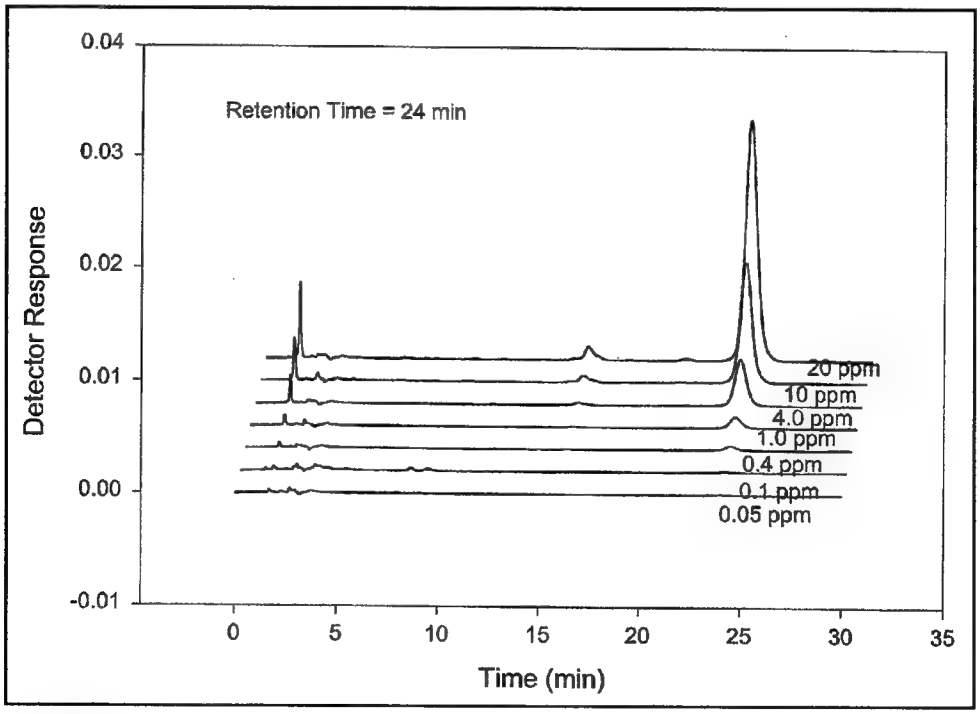

Figure 6. CL-20 calibration on CN column

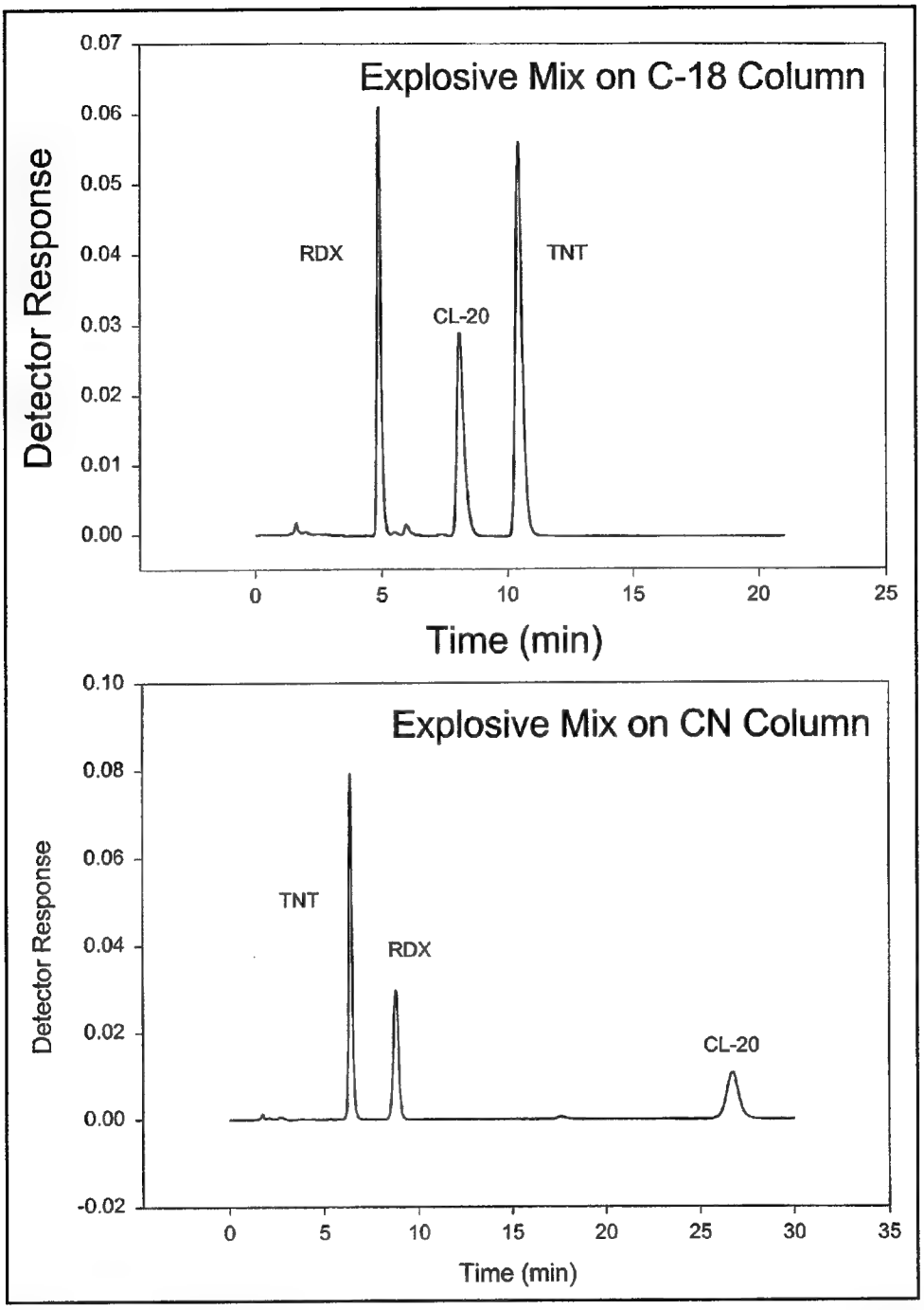

Figure 7. CL-20 separation from other explosives compounds on C18 and CN columns

Table 1
Method Detection Limit (MDL) Statistics for CL-20 in Water and Soil Matrices

Compound	Column	Concentration (ppb)								AVG µg/L	STD DEV	MDL µg/L	% Rec	LRL µg/L
		µg/L	MDL-1	MDL-2	MDL-3	MDL-4	MDL-5	MDL-6	MDL-7					
CL-20 Water	C18	60.00	61.00	58.00	59.00	50.00	53.00	50.00	50.00	54.43	4.79	14.37	90.71	71.86
	CN	60.00	63.00	63.00	54.00	48.00	53.00	53.00	52.00	55.14	5.70	17.10	91.90	85.48
CL-20 SPE	C18	0.60	0.56	0.56	0.56	0.57	0.56	0.53	0.54	0.55	0.01	0.04	92.38	0.21
	CN	0.60	0.60	0.68	0.60	0.60	0.65	0.60	0.60	0.62	0.03	0.10	103.10	0.49
CL-20 Soil	C18	150.00	91.00	94.00	96.00	93.00	92.00	92.00	93.00	93.00	1.63	4.90	62.00	24.49
	CN	150.00	91.00	96.00	120.00	117.00	97.00	110.00	99.00	104.29	11.31	33.93	69.52	169.64

4 Discussion

The ability to measure CL-20 at low levels in waters and soils is an important tool for studying the environmental fate and risks associated with the introduction of CL-20 into the environment. Applications of the technique identified in this report include studies of sorption of CL-20 to soils and sediments, soil column studies to determine the rate of mobility of CL-20 in soils, adsorption/desorption studies to determine groundwater migration rates, CL-20 solubility studies in natural waters, studies of the uptake of explosives by plants, toxicity studies for CL-20, and measurement of rates of natural attenuation of CL-20 in waters and soils. The ability to identify the presence of CL-20 and determine its concentration throughout a specific degradation process provides a means of evaluating each specific remediation technology. It is important to have the capability of accurately and reputably measuring CL-20 in the various compartments identified in an experimental matrix. For example, measurement of CL-20 levels in soil sections, influent water, pore water, and effluent water is necessary when studying the mobility of Cl-20 in a soil column that consists of soil and simulated water moving through the soil. Low detection limits are required for compartments that contain small fractions of the total CL-20 present in the entire system.

The ability to measure CL-20 at low levels in waters and soils is also important in studies of technologies for remediating soil and water contaminated with CL-20. These treatments, analogous to those proposed for remediation of nitroaromatic and nitramines explosives, include biodegradation of CL-20 (Binks, Nicklin, and Bruce 1995), thermal processes for the treatment for mineralization of CL-20 (Funk et al.1993), base hydrolysis for CL-20 transformation (Felt, Larson, and Hansen 2001), phytoremediation (the use of plants) to transform CL-20 (Larson 1997, Larson et al. 1998), advanced oxidation technologies for CL-20 transformation or mineralization (Zappi et al. 1998), physical separation for mass reduction of CL-20 contamination (Olin, Myers, and Townsend 1996), and granulated activate carbon for CL-20 removal from waters.

An example of the effectiveness of the analytical method is shown in Figure 8. This figure contains C18 and CN chromatograms of extracts from CL-20 solutions prior to and following exposure to hydroxide ion in an initial investigation of the potential for base hydrolysis as a low-cost technique for transforming CL-20 in waters and soils. This study shows that a strong base is capable of reducing CL-20 concentrations in water over a period of 18 hours to below the detection limits of the low concentration method used for this study.

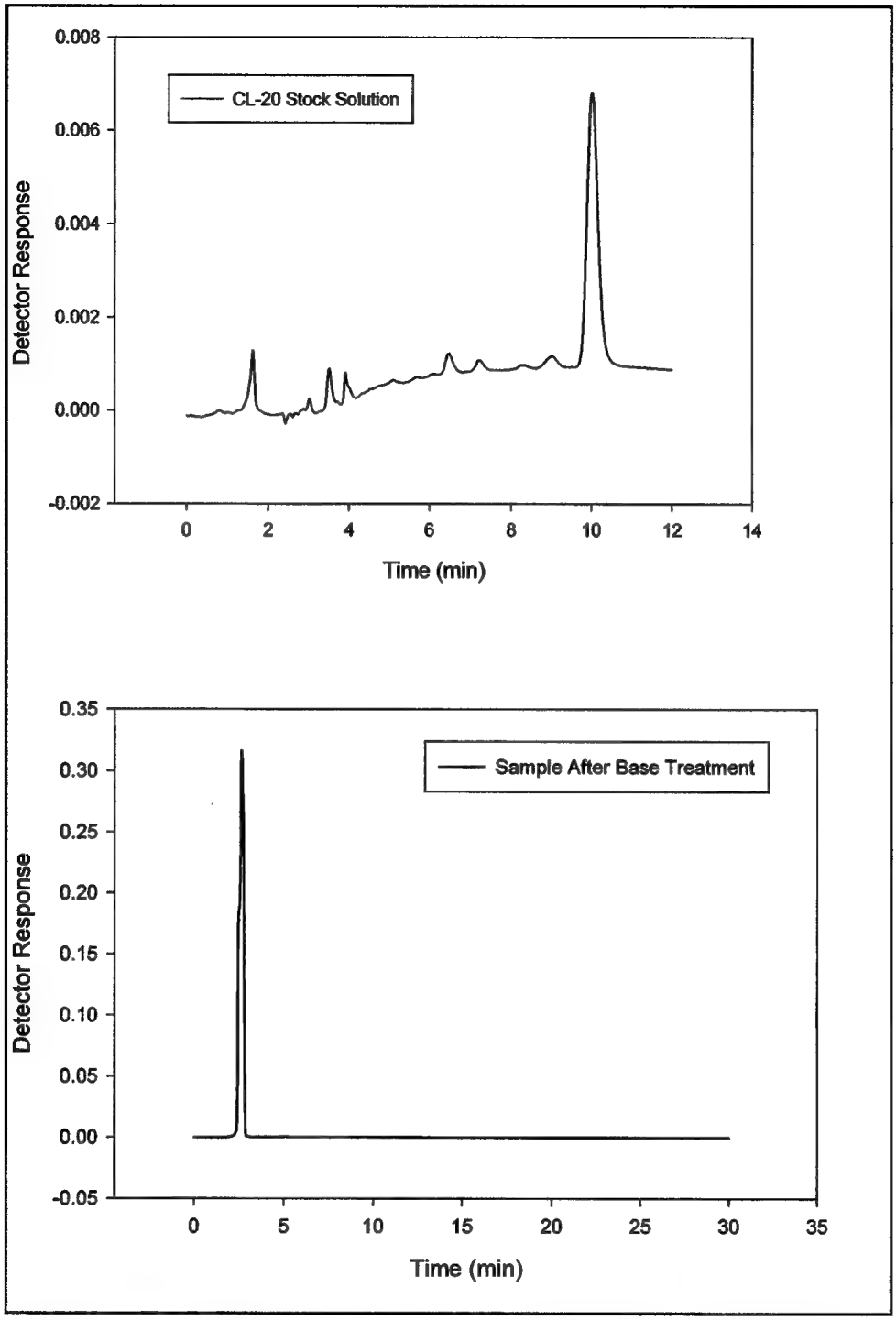

Figure 8. Chromatograms of CL-20 stock and base-treated CL-20 solutions

5 Conclusions

A means of separation and quantitation of the CL-20 in environmental matrices has been developed. This method satisfies the need for analytical techniques to monitor the degradation of CL-20 in remedial systems. The system is based on reverse-phase liquid chromatography for separation of the nitramines. C18 and a CN bonded silica high performance liquid chromatographic columns are used to eliminate common interferences. Contaminant identification is further confirmed by performing a spectral analysis of the compounds upon elution. The method for detecting CL-20 uses techniques and equipment common to most analytical laboratories performing explosives detection. Analytically, it is possible to detect CL-20 down to the 500 parts per trillion range. This analysis technique is relatively simple and cost efficient and is expected to be a valuable tool for evaluating CL-20 contamination.

The usefulness of the technique will depend on how CL-20 is used in weapons system in the future. If its use is similar to that of RDX, TNT, and mixtures of nitramines and nitroaromatics, then the amount of soil and water impacted with this material will be extensive.

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14. ABSTRACT

The determination of new explosive formulations in environmental matrices is necessary for understanding both the environmental threat these compounds present and the effectiveness of remediation technologies for the treatment of contaminated soils and waters. Analytical techniques for the detection of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.05,9.03,11]dodecane (CL-20) in water and soil have been developed. Methods traditionally utilized for the analysis of nitroaromatics were adapted for the determination of CL-20, a cage-like explosive compound. The contaminant of interest is thermally labile, exhibits high polarity, and has low solubility in water. These constraints make the use of specialized sample handling, preparation, extraction, and analysis necessary.

The ability to determine the concentrations of this new explosive compound in environmental matrices is helpful in developing remediation technologies and understanding the fate and effects of CL-20 in the environment. The new method will aid in understanding the physical, chemical, and biological fate of CL-20 once released to the environment. Should it be necessary, the method can be used in developing remediation technology and determining the efficiency of these technologies. The method will aid in

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15. SUBJECT TERMS

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CL-20
Explosives
High performance liquid chromatography
Lime treatment

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14. (Continued).

modeling the toxicological effects of CL-20. The toxicity and mobility of new explosives in soil and groundwater is also of interest, and analytical techniques for quantifying CL-20 and its degradation products in soil and natural waters make these investigations possible. High performance liquid chromatography (HPLC) equipment has been used to separate the compounds produced by the degradation of the cage compound CL-20. HPLC methodology was employed to investigate and develop sample preparation and techniques for analysis of CL-20 in varying matrices.

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